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ABSTRACT: Fuel cells that facilitate electrochemical reactions in the marine environment are under development as future long-term power sources for marine instrumentation. This research focused on anode processes and small-scale environmental impacts of fuel cells operated across sediment-water interfaces in laboratory microcosms and at coastal field sites. Sediment, pore water and electrode surface analyses indicated that electricity production is coupled to the oxidation of dissolved and solid-phase forms of reduced sulfur supplied from the sediments. Sustainable power densities were observed to increase with time under load by 3-6 times compared to yields from graphite electrodes with no history of passing current. Anode modifications, sediment chemical changes, and the associated enhancement of performance suggest fuel cells promote the development of a localized biogeochemical cycle. Bacteria driving the cycle appear to use elemental sulfur as an energy substrate and may transfer electrons within biofilms.

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FINAL REPORT

GRANT #: N00014-02-1-0480

PRINCIPAL INVESTIGATOR: Clare E. Reimers

INSTITUTION: Oregon State University

GRANT TITLE: Energy Harvesting, Electrode Processes and the Partitioning and Speciation of Solid Phase Iron and Sulfur in Marine Sediments

AWARD PERIOD: 15-APR-2002 through 14-APR-2003

OBJECTIVE: To identify the chemical species that may limit energy harvesting by seafloor fuel cells and to determine the processes that may lead to electron transfer to graphite anodes.

APPROACH: Sediment fuel cells that utilize graphite electrodes to facilitate electrochemical reactions between reductants in marine sediments and oxygen in overlying seawater are under development as future long-term power sources for marine instrumentation. Laboratory microcosms containing flowing seawater, natural (but initially sieved and homogenized) anoxic sediments and rod-shaped graphite fuel-cell electrodes were constructed to characterize cell properties and the impacts of electrical power generation. After six-months of continuous electricity production, three microcosms were sampled for measurements of dissolved S(-2), Fe(+2), Mn(+2), sulfate, nutrients, and solid-phase Fe(+3), acid-volatile S (~FeS), pyrite (FeS_2) and total organic carbon as a function of distance from the anodes. Other sediments that were collected from reaction zones above plate-shaped anodes of fuel cells operated (or set out as controls) during 2001 at two coastal demonstration sites in Oregon and New Jersey were treated similarly. Anode surface properties were characterized by scanning electron microscopy and electron microprobe elemental analyses. The major inorganic reductants observed as depleted in the natural sediments were selected for further study as reactants in abiotic anode chambers of two-chambered galvanic cells. These experiments will continue beyond the grant period.

ACCOMPLISHMENTS: We documented that the potential (voltage) of sediment fuel cells develops by establishment of separate equilibrium conditions at both cathode and anode. In general, cell currents are cathode limited initially but shift to anode limitation. Time under load also results in 3-6 times higher sustainable power densities than can be generated with graphite electrodes that have no history of passing current. Recovered anodes exhibit chemical deposits enriched in sulfur and iron at the graphite surface, and these are overlain with biofilms. These results are consistent with 16S DNA studies by Dawn Holmes and co-workers from the University of Massachusetts. They have found that the dominant microorganisms present in anode scrapings are phylogenetically related to a cluster in the delta subclass of the *Proteobacteria* that metabolize elemental sulfur. After months of electricity production, concentrations of dissolved S(-2), Fe(+2) and Mn(+2), and solid-phase acid-volatile S (~FeS), and pyrite (FeS_2) in sediments adjacent to active anodes were impacted. Localized effects on organic carbon, or amorphous or crystalline forms of Fe(+3) could not detected.

Public outreach materials developed during the grant included an interactive display of a seafloor fuel cell within a small aquarium that was highlighted during media events on ONR's test platform for new technologies, AFLOAT lab.

CONCLUSIONS: Electron transfer processes at the anodes of sediment fuel cells result in the oxidation of dissolved and solid-phase forms of reduced sulfur in sediments. These processes become enhanced by the development of a localized biogeochemical cycle involving bacteria that may use elemental sulfur as an energy substrate and may transfer electrons extracellularly within biofilms.

SIGNIFICANCE: Sediment fuel cells have potential for wide application as long duration power sources for marine instrumentation. The studies conducted here have provided a better understanding the available sources of electrochemical energy in sediments, the role of microorganisms in tapping those sources, and the impact of energy harvesting on the sedimentary environment.

PATENT INFORMATION: A patent application for the sediment fuel cell was filed prior to this grant period and has moved closer to being awarded.

AWARD INFORMATION: The authors of the first publication listed below received the 2002 Alan Berman Research Publication Award, from the Naval Research Laboratory.

PUBLICATIONS AND ABSTRACTS:

1. Tender, L.M*., Reimers, C.E*., Stecher, H.A., III, Holmes, D.E., Bond, D.R., Lovley, D.R., Lowry, D.A., Pilobello, K. and Fertig, S. (2002) Harnessing microbially generated power on the seafloor. Nature Biotechnology, 20, 821-825. *corresponding authors.

2. Holmes, D. E., Bond, D.R., O'Neil, R.A., Reimers, C.E., Tender, L.M., Lovley, D.R. (submitted). Microbial communities associated with electrodes harvesting electricity for a variety of aquatic sediments. Applied Env. Microbiol.

3. Lowry, D.A., Tender, L.M., Zeikus, J.G., Park, D. H., Reimers, C.E., Lovley, D.R. (submitted) Harvesting energy from the marine sediment-water interface. II. Kinetic studies on anode materials. Electrochemica Acta.

4. Ryckelynck, N., Reimers, C.E., Stecher, H.A., Holmes, D.E., Bond, D.R. (2002) Bacterial disproportionation of elemental sulfur in a marine sediment amplified by a seafloor fuel cell. EOS abstract B11A-0709. Poster presented at the Annual meeting of the American Geophysical Union.

5. Ryckelynck, N. (in preparation) The seafloor fuel cell mechanism: interactions of graphite anodes with the environment and microbial response. M.S. Thesis, Oregon State University (completion expected spring 2004).